Ocean and Coastal Research

ORIGINAL ARTICLE
Special Article Collection
Carrerette & Bendia (eds), Biology and Geochemistry of seabed pockmark and carbonate mound habitats

http://doi.org/10.1590/2675-2824070.22022ral
ISSN 2675-2824

Characterization of the organic matter in pockmark areas of the Southwestern Atlantic upper slope

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ABSTRACT

Pockmarks are circular or elliptical structures formed at the seabed by the expulsion of gas from the subsurface. They are widely distributed along the continental margin off southeastern Brazil and can be over a kilometer wide and 100 meters deep. However, studies concerning the organic characteristics of these pockmark areas are scarce. This study sought to evaluate the organic composition of the sedimentary matter in pockmark areas located in the continental slope region of the southern Brazilian coast. Hydrocarbons, sterols, long-chain alcohols, stable isotopes of C and N, total organic carbon, and total nitrogen were assessed to provide an organic molecular characterization of the pockmarks located in the Southwestern Atlantic Ocean. These compounds did not reflect the organic characteristics of the scape of fluids that generate pockmark structures.

Descriptors: Sediment, Hydrocarbons, Stable isotopes, Sterols, Alcohols.

INTRODUCTION

Pockmarks are crater-like structures found on the seabed formed due to the sudden release of pressurized subsurface gas or pore water through sediments (King and MacLean, 1970; Cathles et al., 2010). Their presence has been described in different geographical locations (Brothers et al., 2011) and depths (King and MacLean, 1970; Gay et al., 2006; Brothers et al., 2011), and their structure may act as traps, promoting the accumulation of ancient sediments (Ramos et al., 2020). Hydrodynamics and sedimentary processes influence the deposition and conservation of sedimentary organic matter inside and around the pockmarks in different ways, especially in sites with high sedimentation rates and more significant deposition of organic matter (de Mahiques et al., 2004).

Submitted: 24-March-2022
Approved: 12-July-2022

Associate Editor: Amanda Bendia

In the southeastern Brazilian coast, Calder et al. (2002) described the first signs of pockmarks in the Santos Basin. These structures, which can exceed 1 km in diameter and 100 m in depth below the rim, are subject to different hydrodynamic and sedimentary processes (Schattner et al., 2016; de Mahiques et al., 2017; Ramos et al., 2020). Although direct signs of gas leakage have not yet been observed, Sumida et al. (2004) identified the possibility of periods of pockmark activity due to the numerous benthic fauna found. Miller et al. (2015) reported evidence of methane production in pockmarks found in the Pelotas Basin in southern Brazil.

The organic compounds from pockmark sediment may indicate different responses for the diagenesis of the organic matter. According to Boitsov et al. (2011), different responses for the origin of organic matter between the inner and outer areas of a pockmark in the Barents Sea (Norway) indicate episodes of hydrocarbon exudation from deeper layers of sediment to the surface. Nickel et al. (2013) conducted another study in the Barents Sea and found a mixture of biogenic and thermogenic hydrocarbons where petrogenic compounds were present. The authors related them to erosive processes and diagenesis of petrogenic material instead of active exudations of hydrocarbons. Haverkamp et al. (2014) studied inactive pockmarks on the Norwegian Oslofjord and found that surface sediments of inactive pockmarks are indistinguishable from surrounding sediments. However, different structures were found at 40 cm depth compared to surrounding sediments.

The evaluation of the sedimentary content of pockmarks is important because their depressions may act as traps and promote the accumulation of ancient sediments (Haverkamp et al., 2014, Ramos et al., 2020), and their presence may be related to hydrocarbon reservoirs (Hovland et al., 2002). However, no studies have been published relating elementary and organic compounds to the sources of organic matter in sediment samples from pockmarks in the Brazilian coast.

The present study aims to assess the levels and sources of organic compounds, carbonate contents, and stable isotopes on the pockmark areas on the Brazilian Coast. Aliphatic and polycyclic aromatic hydrocarbons, sterols, n-alcohols, stable isotopes of carbon ($\delta^{13}C$) and nitrogen ($\delta^{15}N$), total organic carbon (TOC), and total nitrogen (TN) were analyzed from sedimentary columns and superficial sediments of different pockmarks fields located in the Santos Basin.

METHODS

Study Area

The study area is comprised of pockmark fields in the southern part of the Santos Basin (Fig. 1). A prior multibeam survey conducted aboard the R/V Sirius of the Brazilian Navy in 2011 covered an area of 106 × 29 km of the Santos shelf break and upper slope. Data analysis revealed 984 pockmarks, with diameters of up to 1 km and depths below the rim of up to 230 m (Schattner et al. 2016; de Mahiques et al. 2019). Further campaigns sampled sediments inside and outside the pockmarks (dos Santos et al. 2018). These authors recognized distinct grain size and abundance of bioclasts inside and outside the pockmarks.

Sampling and analytical procedures

The sampling areas were determined through seismic profiles acquired with an acoustic profiler of the Chirp type (3.5 kHz) to identify pockmark morphology and location. Bubbles were not observed during seismic survey, suggesting that there was no leakage of fluids during sampling. The sediment from sixteen sampling points (Fig. 1 – Table 1) were collected from 2015 to 2018 using a Box Core (dimensions 50 cm x 50 cm x 60 cm), at eight sampling points (#253 to #255, #257, #265, #267, #690, and #691). Cores were sub-sampled continuously at 2-cm intervals, immediately frozen, and later freeze-dried. At the sampling points #586 to #589, #591 to #593, and #689, only the superficial sediments were considered for this work.

Calcium Carbonate and Bulk Organic Matter Analysis

The calcium carbonate content was determined by gravimetric analyses of the weight difference before and after sample acidification with 2M HCl. Total organic carbon, total nitrogen, and $\delta^{13}C$

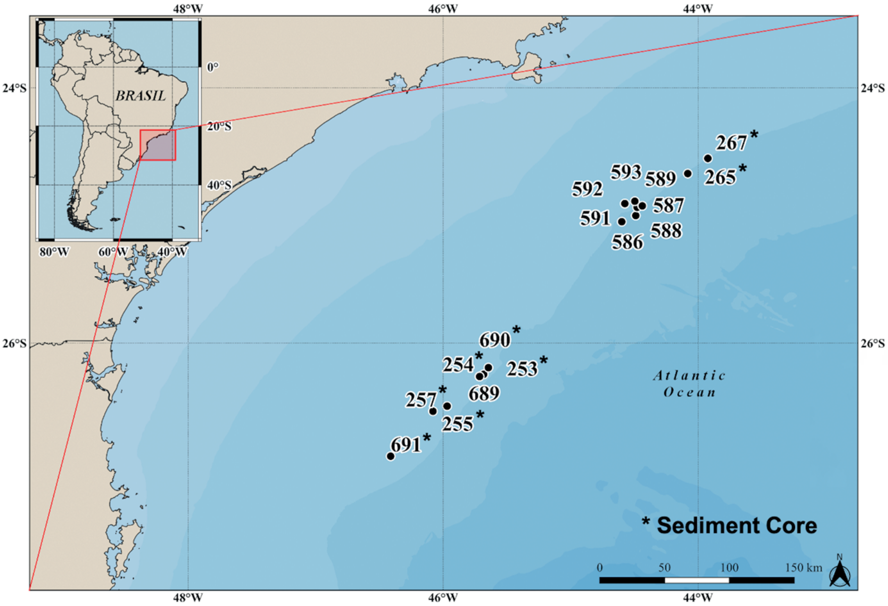

Figure 1. Location of the study area and sampling stations. *Sediment cores.

Table 1. Location of the sampling points over the pockmarks areas and parameters analyzed.

Sampling Point	Latitude (S)	Longitude (W)	Depth (m)	Aliphatic Hydrocarbons	Polycyclic Aromatic Hydrocarbons	Sterols	n-Alcohols	TOC, TN,$CaCO_3$; and $\delta^{13}C$ $\delta^{15}N$
253	26°14.72’	045°40.97’	731	every 2 cm	-	every 2 cm	every 2 cm	every 2 cm
254	26°15.72’	045°42.97’	747	every 2 cm	-	every 2 cm	every 2 cm	every 2 cm
255	26°29.68’	045°58.15’	652	every 2 cm	-	every 2 cm	-	every 2 cm
257	26°32.08’	046°04.82’	543	every 2 cm	-	every 2 cm	every 2 cm	every 2 cm
265	24°40.3T	044°04.89’	818	every 2 cm	every 2 cm	-	every 2 cm	every 2 cm
267	24°33.18'	043°55.43’	805	every 2 cm	every 2 cm	-	every 2 cm	every 2 cm
586	25°02.97’	044°35.95’	1009	0-2 cm only	-	-	-	0-2 cm only
587	25°00.06’	044°29.36’	1070	0-2 cm only	-	-	-	0-2 cm only
588	24°56.19’	044°28.72’	663	0-2 cm only	-	-	-	0-2 cm only
589	24°55.51’	044°26.28’	780	0-2 cm only	-	-	-	0-2 cm only
591	24°54.49’	044°34.53’	547	0-2 cm only	-	-	-	0-2 cm only
592	24°54.43’	044°34.51’	535	0-2 cm only	-	-	-	0-2 cm only
593	24°53.32’	044°29.81’	563	0-2 cm only	-	-	-	0-2 cm only
689	26°15.74’	045°42.87’	592	0-2 cm only	0-2 cm only	0-2 cm only	0-2 cm only	0-2 cm only
690	26°11.56’	045°38.73’	592	2 cm interval	2 cm interval	2 cm interval	2 cm interval	2 cm interval
691	26°53.22’	046°24.73’	592	2 cm interval	2 cm interval	2 cm interval	2 cm interval	2 cm interval

(reported in ‰ PDB) analyses were performed with an elemental analyzer (EA - Costec) coupled to the isotopic ratio mass spectrometer (IRMS - Delta Advantage – Thermo Scientific) after total elimination of calcium carbonate from the samples using 2M HCl. $\delta^{15}N$ (reported in ‰ Air) was also analyzed by EA-IRMS using non-decarbonated samples.

Organic compounds analysis

In the sediment samples, a group of seven sterols were selected for analysis: (1) C27 sterols: cholestanol (5α(H)-cholestan-3β-ol—$27\Delta^0$), cholesterol (cholest-5-en-3β-ol—$27\Delta^5$); (2) C28 sterols: brassicasterol (24-methylcholest-5,22-dien-3β-ol -$28\Delta^{5,22E}$), campesterol (24-methylcholest-5-en-3β-ol - $28\Delta^5$); (3) C29 sterols: stigmasterol (24-ethylcholest-5,22(E)-dien-3β-ol—$29\Delta^{5,22E}$), β-sitosterol (24-ethylcholest-5-en- 3β-ol - $29\Delta^5$), and β-sitostanol (24-ethyl-5α-cholestan-3β-ol -$29\Delta^0$). *n*-Alcohols from *n*-C_{12} to *n*-C_{30} were considered. The analyzed hydrocarbons consisted in the 16 EPA-priority PAH further than dibenzothiophene, benzo[e]pyrene, and alkylated homologues (C1–C4-naphthalenes, C1–C3-fluorenes, C1–C3-dibenzothiophenes, C1–C4-phenanthrenes–anthracenes, C1–C2-fluoranthenes-pyrenes, C1–C2-chrysenes), and the aliphatic hydrocarbons (*n*-alkanes *n*-C_{12} to *n*-C_{36}, pristane, phytane).

The analytical procedure for the organic compounds (AHs, PAHs, *n*-alcohols and sterols) analysis was similar to that reported by Lourenço et al. (2021). Twenty grams of freeze-dried sediment were 8-h Soxhlet extracted with 80 ml of dichloromethane-hexane (1:1, v:v). The surrogates 5α-androstanol (for sterols and *n*-alcohols), naphthalene-d_8, acenaphthene-d_{10}, phenanthrene-d_{10}, chrysene-d_{12} and perylene-d_{12} (for PAH), and 1-hexadecene and 1-eicosene (for AHs) were added prior extraction to each sample. The concentrated extracts (1 ml) were introduced to an adsorption chromatography column with 2 g of 95% activated alumina. Elution was performed using 10 ml of a mixture (3:7) of *n*-hexane:dichloromethane (fraction 1 – AH and PAH) and 15 ml of (1:1) *n*-hexane:methanol (fraction 2 – *n*-alcohols and sterols). The extracts from fraction 1, AH, and PAH were concentrated to 0.5 ml. The extracts from fraction 2, *n*-alcohols, and sterols were evaporated to dryness and derivatized to form trimethylsilyl ethers using 40µl of bis(trimethylsilyl)trifluoroacetamide (BSTFA) with 1% trimethylchlorosilane (TMCS) for 90 min at 65 °C. After BSTFA/TCMS was evaporated to dryness, and fraction 2 was recovered in *n*-hexane (0.5 ml). Internal standards, 1-tetradecene (AH), ρ-terphenyl-d_{14} (PAH), and 5α-cholestane (*n*-alcohols and sterols), were added before chromatographic analyses.

N-alkanes (from *n*-C_{10} to *n*-C_{40}), pristane, and phytane analyses were performed using an Agilent GC (model 6890) equipped with a flame ionization detector (FID) and an HP-5 fused silica column (Agilent 19091J-015, 50 m length, 0.32 mm ID, and 0.17 µm film thickness). Hydrogen was used as the carrier gas. The injector temperature was adjusted to 300 °C, and splitless injection was adopted. The oven temperature was programmed to start at 40 °C and hold for 1.5 min and then increase to 325 °C at 10 °C min^{-1}, holding at 325 °C for 10 min. The PAH analyses were performed using an Agilent GC model 6890N coupled to an Agilent single quadrupole (MS) model 5973N equipped with HP5-MS capillary fused silica column (Agilent 19091S-433, 30 m length, 0.25 mm ID, 0.25 µm film thickness). Helium was used as a carrier gas. The injector temperature was adjusted to 300 °C, and splitless injection was adopted. The oven temperature was programmed to start at 40 °C and hold for 2 min, from 40 to 100 °C at 25 °C min^{-1}, from 100 to 230 °C at 5 °C min^{-1}, from 230 to 270 °C at 2 °C min^{-1} holding at 270 °C for 5 min, and finally to 300 °C at 5 °C min^{-1}. Sterols and *n*-alcohols analyses were performed using an Agilent gas chromatograph (GC) model 7890B coupled to an Agilent triple-quadrupole (TQMS - model 7010B). Separations were achieved with an HP5-MS capillary fused silica column (Agilent 19091S-433UI, 30 m length, 0.25 mm ID, 0.25 µm film thickness). Helium was used as the carrier gas. The oven temperature was programmed from 40 to 240 °C at 10 °C min^{-1}, then 245 °C at 1.0 °C min^{-1}(holding for 5 min), and finally 300 °C at 4°C min^{-1} (holding for 5 min). The injector temperature was adjusted to 300 °C, and splitless injection was adopted.

Compounds were identified by matching the retention times with the results from standard compounds and by the ion mass fragments (m/z) when GC-TQMS and GC-MS were adopted. Individual compound concentrations were obtained using the surrogate standard peaks area method and 5-point analytical curves for individual components.

Procedural blanks (calcined Na_2SO_4) analyses were performed at the same extraction batch of the samples, and no peaks interfered with the analyses of the target compounds. The recoveries of the surrogates, considering all samples and all classes of compounds, ranged from 70 to 105%. A spike-recovery experiment (spiked blank and spiked sediment sample) was conducted during the extraction of the samples, and the recoveries of the spiked compounds, of all classes of compounds, ranged from 63 to 98%. Detection limits (DL) calculated, in dry weight, were 1.0 ng g^{-1} for AH, 0.12 ng g^{-1} for PAH, and 10 ng g^{-1} for sterols.

DATA ANALYSIS

The parameters analyzed in the sampling points are presented in Table 1. The individual cores and the superficial sediments were screened for spatial variability in the sources of organic matter and for variations along the sedimentary column.

RESULTS AND DISCUSSION

The full set of results is presented in the Supplementary Material (Table S1).

CALCIUM CARBONATE AND BULK ORGANIC MATTER

The comparison of carbonate contents in the sedimentary cores of the different sampling points presented significant variations (Fig. 2A). However, along with the sediment cores, the content of carbonate was uniform. The sediment from cores #253, #254, #255, and #257 presented the highest carbonate content, with mean values and standard deviation of 30.5±2.7%, 25.1±2.4%, 38.6±1.9%, and 26.0±1.1%, respectively. Although core #690 was nearby cores #253 and #254, its carbonate content was lower at 3.5±0.4%, similar to the content found in core #691 (3.5±1.3%). Cores #265 and 267 were found to have lower carbonate contents, 0.9±0.2% and 0.8±0.2%, respectively.

The TOC content along the sediment cores ranged from 0.1 to 1.0% (mean 0.6±0.2%). The highest TOC content was found in core #257 (mean 1.0±0.6 %), with the lowest at core #691 (mean 0.4±0.3%) (Fig. 2B). The TOC content is similar to those found in other pockmarks around the world (Haverkamp et al., 2014). Total nitrogen in the sediment cores varied from 2.1 to 7.4 % (mean 5.5±0.8 %) (Fig. 2C). TN content was higher than that reported in other pockmark areas (Håvelsrud et al., 2012; Haverkamp et al., 2014).

TOC and TN provide important information about sedimentary organic matter. The organic matter produced by terrigenous and marine photosynthetic organisms provides a distinct C/N ratio, mainly due to the different contributions of their structural components (Meyers, 1994). Typically, marine organic compounds present C/N ranging from 4 to 10. Meanwhile, terrigenous sources produce C/N greater than 20 (Meyers, 1994). The mean value of C/N, considering all cores, was 6.4±1.5, indicating marine primary production as the main source of organic matter to the areas.

The results of the stable isotopes ($\delta^{13}C$ and $\delta^{15}N$) support the source of organic matter suggested by the C/N ratio. Results of $\delta^{13}C$ and $\delta^{15}N$ in the cores ranged, respectively from -21.0 to -19.3 ‰ (mean -21.0±0.5‰) and from 2.1 to 7.4 ‰ (mean 5.5±0.7‰) (Fig. 2 D and E). Typically, $\delta^{13}C$ values are found between -22 and -20 ‰ for organic matter produced by marine organisms and between -24 and -31 ‰ for terrigenous organic matter (Meyers, 1994). The δ15N of terrestrial vascular plants ranges from –5‰ to 18‰ (3‰ average), whereas that of marine organic matter ranges from 3‰ to 12‰ (6‰ average) (Wada and Hatori, 1990). These results indicate a prevalence of marine organic matter for all sampling points. Considering that the sampling sites are more than 250 km from the coast at depths ranging from 535 to 1070 m, a significant contribution of terrigenous organic matter was not expected.

ALKANES

The total *n*-alkanes, pristane, and phytane contents in the sediment cores ranged from 21.6 to 701.1 ng g^{-1} (mean 271.6±137.8 ng g^{-1}). The highest alkanes contents were found at cores #253 to #255, with the lowest at #690 and #691 (Fig. 3A). As reported for the carbonate and TOC contents, a significant difference in alkanes levels was observed despite the proximity of cores #253 and #254 to #690 (Fig. 3A).

Bacteria, algae, and higher plants produce *n*-alkanes with different lengths of carbon chains. Short carbon chains with an odd number of carbon atoms, generally between *n*-C_{15} and *n*-C_{19}, characterize algae sources. Meanwhile, long carbon

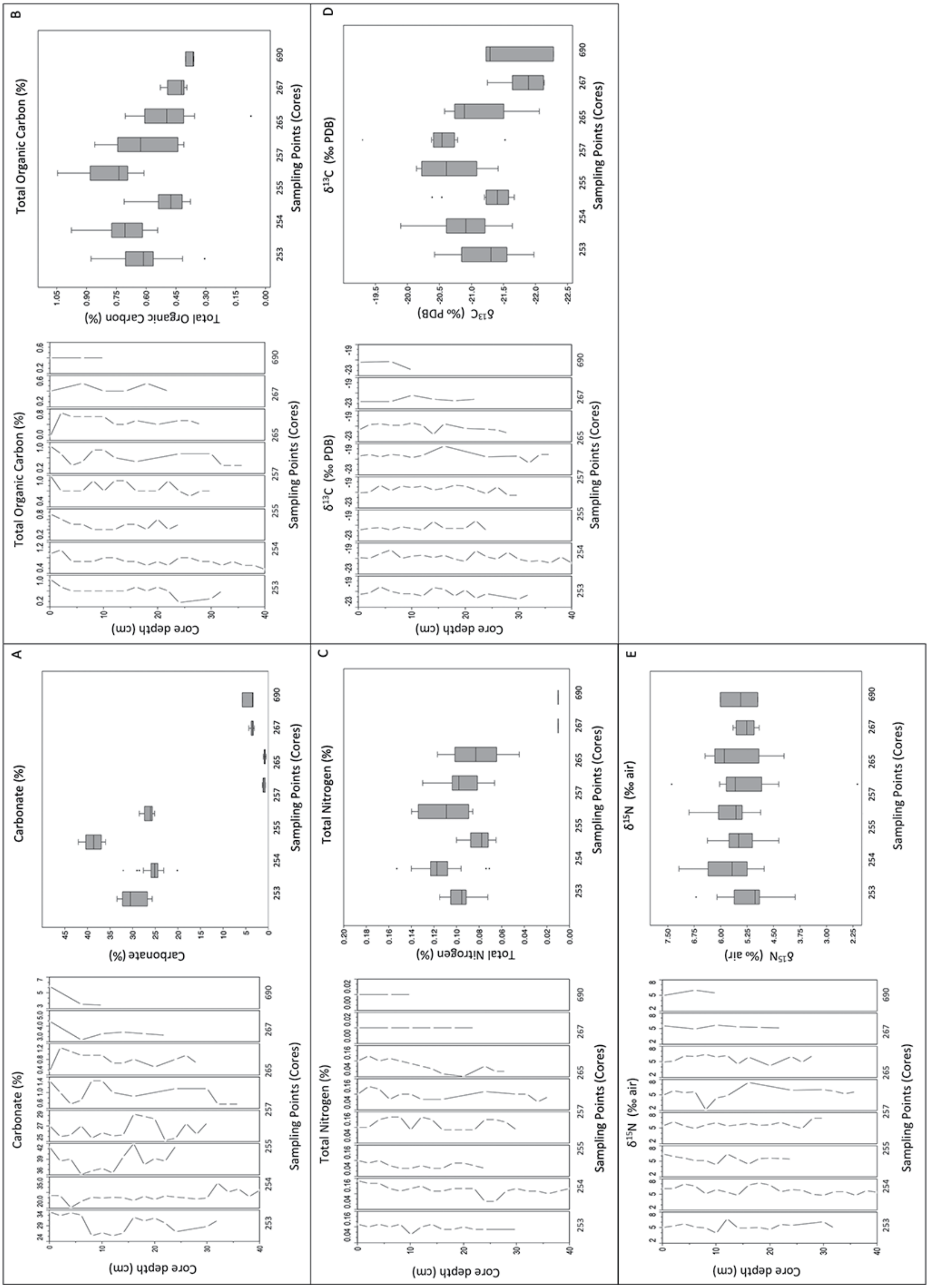

Figure 2. Pattern (left side) and Boxplot (right side) of the contents of (A) carbonate (%), (B) total organic carbon (%), (C) total nitrogen (%), (D) $\delta^{13}C$ (‰ PDB), and (E) $\delta^{15}N$ (‰ air) in the sediment cores #253, #254, #255, #257, #265, #267, #690, and #691. (* represent the outlier values).

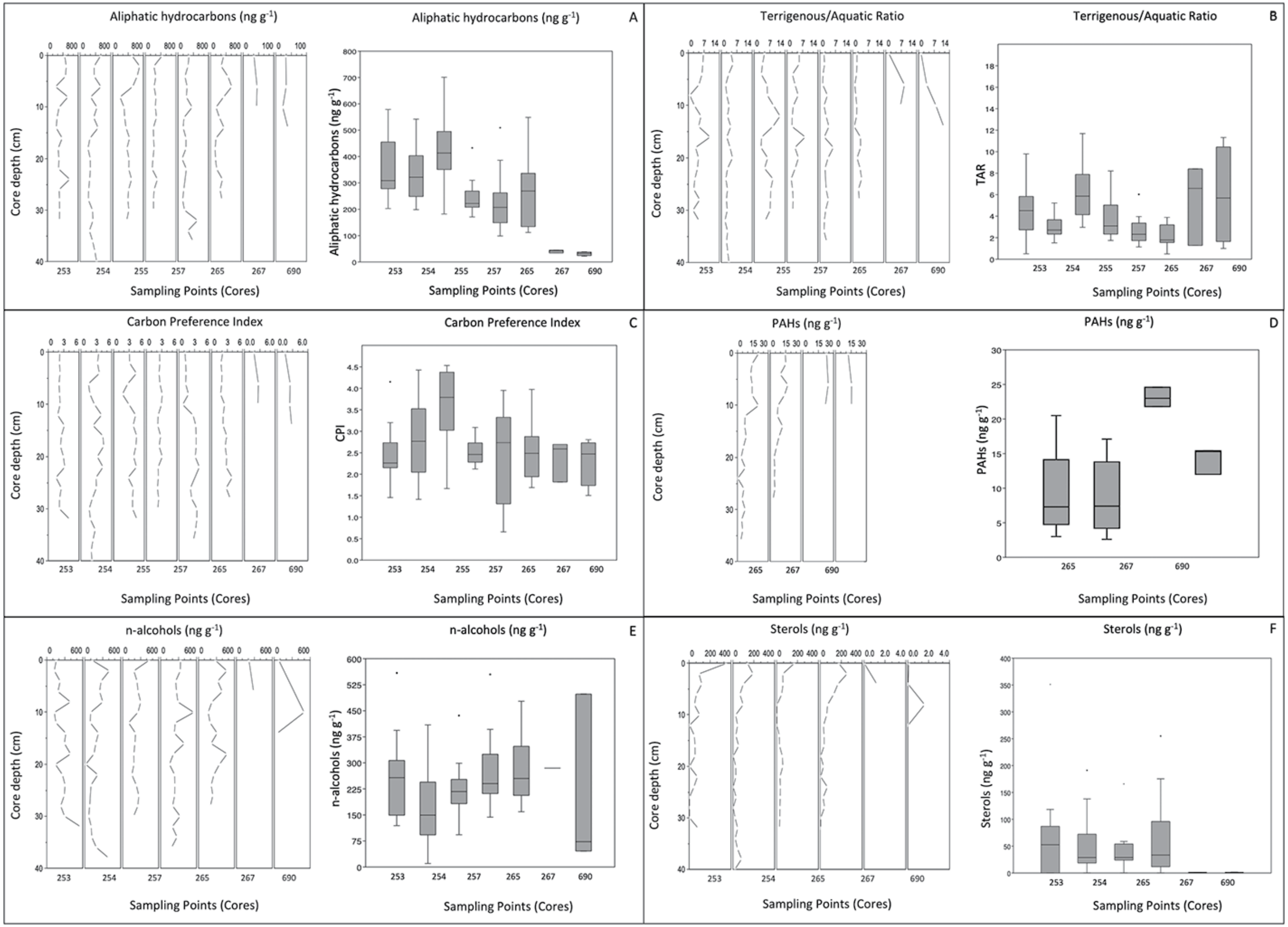

Figure 3. Pattern (left side) and Boxplot (right side) of the contents of (A) Aliphatic Hydrocarbons (ng g^{-1}), (B) Terrigenous/Aquatic Ratio, (C) Carbon Preference Index; (D) Polycyclic Aromatic Hydrocarbons (ng g-1). and (E) n-Alcohols (ng g^{-1}) in the sediment cores #253. #254, #255, #257, #265, #267, #690, and #691. (* represent the outlier values). $\mathrm{TAR} = \frac{n\text{-}C_{27}+n\text{-}C_{29}+n\text{-}C_{37}}{n\text{-}C_{15}+n\text{-}C_{17}+n\text{-}C_{19}}$ $CPI = \frac{1}{2}\left(\frac{n\text{-}C_{25}+n\text{-}C_{27}+n\text{-}C_{29}+n\text{-}C_{31}+n\text{-}C_{33}}{n\text{-}C_{24}+n\text{-}C_{26}+n\text{-}C_{28}+n\text{-}C_{30}+n\text{-}C_{32}} + \frac{n\text{-}C_{25}+n\text{-}C_{27}+n\text{-}C_{29}+n\text{-}C_{31}+n\text{-}C_{33}}{n\text{-}C_{26}+n\text{-}C_{28}+n\text{-}C_{30}+n\text{-}C_{32}+n\text{-}C_{34}}\right)$

chains, between *n*-C_{27} and *n*-C_{35} carbon atoms, characterize higher plants sources (Eglinton and Hamilton, 1967; Young-blood et al., 1971). Based on these differences, some diagnostic ratios such as the terrigenous/aquatic ratio (TAR) and the carbon preference index (CPI) were proposed to distinguish terrestrial and marine sources in marine sediment (Bray and Evans, 1961; Bourbonniere and Meyers, 1996). TAR values close to or lower than 1 may be attributed to the predominance of aquatic sources, while higher values may be attributed to the predominant terrestrial origin (Bourbonniere and Meyers, 1996). In the present work, the TAR values ranged from 0.5 to 11.7 along with the sediment cores (Figure 3B). In 66% of the samples, TAR values were lower than 4.0 (mean 3.2±2.3). CPI values close to 1 found in pockmark regions may be related to the presence of thermogenic hydrocarbons (Boitsov et al., 2011; Nickel et al., 2013). Values greater than 1 reflect the predominance of odd over even *n*-alkanes and may be related to terrigenous sources. In the studied area, CPI values ranged from 0.7 to 4.5 (Figure 3C). In 82% of samples, CPI values were higher than 2.0 (mean 2.6±0.8). For most samples, both TAR and CPI values, observed along with the cores, were similar and close to the limits for defining the origin of organic matter stipulated for diagnostic indeces. Though their interpretation may be dubious because they are in the boundary, these values most likely suggest the predominance of marine organic matter sources in the area. The predominance of the marine source is also supported by the significant contribution of *n*-C_{12} and *n*-C_{14} counterparts to total *n*-alkanes observed in most cores. These *n*-alkanes are, unlike odd-chain *n*-alkanes, generally derived from marine bacteria in oxide environments (Nishimura & Baker, 1986).

The contents of the aliphatic hydrocarbons found in these pockmark areas were lower than those reported by Lourenço et al. (2017a) along the same continental shelf (Σ*n*-alkanes: 1430 to 9280 ng g^{-1}), despite the assumption that pockmarks could act as organic matter traps. However, the TAR and CPI values found in the pockmark areas and along the continental shelf were in the same range, suggesting that the processes that control sediment deposition in the pockmark areas are similar to those found along the continental shelf. Håvelsrud et al. (2012) suggested that the low content of aliphatic hydrocarbons in pockmark areas could also be attributed to methanotrophic organisms capable of promoting the degradation and oxidation of hydrocarbons to CO_2. Many hydrocarbon-degrading prokaryotes have been described, mainly from the Alpha-, Delta-, and Gamma-proteobacteria class and Firmicutes-phylum (Yakimov et al., 2007; Håvelsrud et al., 2012; Jaekel et al., 2013). Members of these groups can degrade complex mixtures of hydrocarbons (Meckenstock and Mouttaki, 2011; Rosenberg, 2013; Abbasian et al., 2015; Giovannelli et al., 2016). Despite this possibility, the low content of alkanes in these pockmark areas of the Southwestern Atlantic upper slope are more likely associated with the low TOC contents.

POLYCYCLIC AROMATIC HYDROCARBONS

The PAH content along the sediment cores (#265, 267, #690, and #691) was relatively low, ranging from 3.0 to 20.5 ng g^{-1} (mean 7.3±5.6 ng g^{-1}) (Fig. 3D). These low levels are comparable to remote areas such as Antarctica (Martins et al., 2004) and can be deemed background levels. However, within 10 cm of the top of the cores, the PAH content was higher than in the older sediments. It is not possible to determine the origin of these compounds because their content is close to the detection limit of the analytical method, thus generating uncertainties in the diagnostic indices such as those proposed by Yunker et al. (2002). The low PAH content could also be related to the low TOC content, as suggested by the alkanes.

LONG-CHAIN *N*-ALCOHOLS

The total long-chain alcohols content in the sediment cores ranged from 10.1 to 558.9 ng g^{-1} (mean 228.9±110.5 ng g^{-1}). Despite variations across and between the different sediment cores (Fig. 3E), the pattern of *n*-alcohols were dominated by long-chain compounds with an even number of carbons in the carbon chain, mainly *n*-$C_{28\text{-}OH}$ and *n*-$C_{30\text{-}OH}$, followed by *n*-$C_{16\text{-}OH}$. Usually, the predominance of *n*-alcohol sources in the marine sediment can be inferred through the length of the carbon chain; terrigenous sources generally produce longer carbon chains than marine sources (Fernandes et al., 1999; Muri et al., 2004; Mudge et al., 1999). Nevertheless, in most cores, the content of most *n*-alcohols was below the detection limit, and the assessment based on the length of the carbon chain is thus uncertain.

STEROLS

The content of total sterols in the cores ranged from undetected to 351 ng g^{-1} (mean 31.9±61.4 ng g^{-1}) (Fig. 3F). These concentrations were lower than those found by Yoshinaga et al. (2008) (730 to 16,800 ng g^{-1}) and Lourenço et al. (2017b) (2250 - 5810 ng g^{-1}) in superficial sediments from shallow offshore areas, up to 100 m depth water column. The highest contents were found in the upper top samples and, as reported for the other parameters, the sterol content in cores #690 and #691 was the lowest found despite their proximity to other sampling points (Fig. 3F). Most sterols were not found in any samples. Cholestanol, cholestanone, and stigmasterol represent almost the totality of sterols analyzed, but were not found in every sample. Generally, these sterols are more associated with terrigenous sources than with marine productivity (Killops & Killops, 2013). However, the diagnostics of the source of the organic matter based on sterols are not reliable due to the non-detection of most compounds.

CONCLUSION

The concentrations of all organic compounds were low and could be deemed background levels. This seems to contradict the assumption that pockmarks could act as organic matter traps. However, through the compounds and parameters used in this work, it was not possible to identify any organic signature that would be left by the escape of gas that formed the pockmarks. Combined, this leads to some possibilities that could explain the organic characterization: (1) the long chain organic compounds, such as those evaluated in this work, do not reflect the organic characteristics of the escape of fluids that generate a pockmark structure. This is supported by most of the diagnostic indices that suggested primary productivity as the main source of organic matter in the sediment, not hydrocarbon-rich fluid; (2) the possible abundance of methanotrophic organisms present in the pockmarks may be capable of promoting the degradation and oxidation of hydrocarbons; and (3) these sites are inactive or have not been active in the recent past, and the any signature from the escape of gas and fluids based on long-chain organics compounds have been lost.

ACKNOWLEDGMENTS

ANP and Shell Brasil supported this work through the R&D levy regulation within the Bioil Project (Biology and Geochemistry of Oil and Gas Seepages, SW Atlantic) and São Paulo Research Foundation - FAPESP (grants No. 2014/08266-2 and No. 2015/17763-2). The authors are indebted to the crew and researchers who participated in surveys aboard the R.V. Alpha Crucis for their constant support. RAL acknowledges the Brazilian National Research Council (CNPq grant no. 308136/2020-9). MMM acknowledges CNPq (research grant 300962/2018-5). This study was financed in part by the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior - Brasil (CAPES) - Finance Code 001. The authors also thank FAPESP, Process No. 2016/18348-1 for the use of the GC-TQMS.

AUTHOR CONTRIBUTIONS

R.A.L.: conceptualization, methodology, investigation, writing, and editing;

N.A.K., D.N., C.A.M.: methodology, investigation, and writing;

A.D.S.P., B.M.T.S.N., C.T.T., F.R.S., G.A.P., L.D.A., L.S.N., N.F.C., J.S., S.T., M.M., M.C.B.: investigation and writing;

P.Y.G.S.: conceptualization and writing.

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